

TRANSLATION 97-4-62

(19) Japan Patent Office (JP)

(11) Patent Number
No.: 2586575

(12) Patent Official Gazette (B2)

(45) Publication date: 3/5/1997

(24) Registration date: 12/5/1996

| (51) Int. Cl ^P | I.D. No. | Interbureau Classification No. | F1 |
|---------------------------|----------|--------------------------------|-------------------|
| G 11 B 7/24 | 526 | 8721-5D | G 11 B 7/24 526 N |
| C 08 K | 5/00 | KFL | C 08 K 5/00 KFL |
| C 08 L | 23/20 | KER | C 08 L 23/20 KER |
| | 25/00 | KFY | C 08 L 25/00 KFY |
| | | KGB | KGB |
| /(C 08 K | 5/00 | | |
| | 5:13 | | |
| | 5:49) | | |

Number of claims: 4 (6 pages)

(21) Application No. S63-125481

(22) Application Date: 5/23/1988

(65) Kokai No. : Patent Application Kokai H1-294753

(43) Kokai date: 11/28/1989

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(54) [Title of the Invention]

Optical Disc Substrate

(56) References:

Patent Application Kokai No. S61-268744 (JP, A)

Patent Application Kokai No. S61-138648 (JP, A)

(57) [Scope of the Patent Application]

[Claim 1]

Optical disc substrate characterized by the fact that it consists of the poly vinyl cyclo hexane type resin which is blended with a hindered phenol type heat stabilizer and a phosphorus type heat stabilizer, of which the 5 % weight loss temperature measured by the thermo gravimetric analyzer is 295 °C or higher.

[Claim 2]

Optical disc substrate characterized by the fact that the hindered phenol type heat stabilizer has 4 or more hindered phenol groups per molecule, as was described in Claim 1.

[Claim 3]

Optical disc substrate characterized by the fact that the phosphorus type heat stabilizer is, tetra kis (2, 4- di- t- butyl phenyl) -4, 4'- bi-phenylene phosphonite and / or bis (2, 6- di- t- butyl -4- methyl phenyl) penta erythritol -di- phosphite, as was described in Claim 1 or Claim 2.

[Claim 4]

Optical disc substrate characterized by the fact that the number average molecular weight of the poly vinyl cyclo hexane type resin is 40,000 to 300,000, as was described in any one of Claim 1 to Claim 3.

[Detailed Explanation of the Invention]

[Field of Utilization in Industry]

This invention relates to the optical disc substrate, in particular, it relates to the optical disc substrate which includes a specific heat stabilizer, and which consists of the poly vinyl cyclo hexane type resin which has excellent heat processing stability.

[Existing Technique]

The optical recording that uses a laser, can record, store and regenerate the high density information, therefore, its development has been aggressively practiced. The optical disc can be listed as an example of optical recording like this. Generally, the optical disc is constructed basically with a transparent substrate, and the various recording media that were coated on top of it.

The colorless transparent synthetic resin is commonly used for the optical disc, and its representatives are the poly carbonates (from now on these will be abbreviated as PC.) or poly methyl methacrylate (from now on this will be abbreviated as PMMA.). These resins have excellent natural characteristics in addition to the lack of color and good transparency, however, they do not meet all the requirements to be the optical materials, especially as the optical disc substrate, and they have problems that must be solved. For example, PC has a birefringence problem due to the aromatic ring, and there are some problems with the moisture absorbency and the water permeability too.

On the other hand, the problems with the heat resistance, the moisture absorbency, and the toughness have been considered for a long time in PMMA.

Thus, these resins have their own problems, however, in actual cases, there are more problems in relation to the recording medium which will be coated on the transparent substrate made out of these resins, and this new problem will be described later.

On the other hand, people are working widely to develop the recording medium,

matched to the usage of the optical discs. For example, in the write once type, which is strictly for the use of the recording - regenerating only, the hole making type is known. In the erasable type, which is for the use as the recording - regenerating - erasing - re-recording media, the phase transition type one which utilizes the crystal transformation phenomenon, and the photo magnetic type one which utilizes the photo magnetic effect, etc., have been known. Concerning the materials for these recording media, mainly the inorganic type materials are used, for example, tellurium or its oxide, alloy compounds, etc., are used in the write once type, and the amorphous alloy compounds of the rare earth - transition metals such as $\text{Gd} \bullet \text{Fe} / \text{TbFe}$, $\text{Gd} \bullet \text{Fe} \bullet \text{Co} / \text{Tb} \bullet \text{FeCo}$, etc., are used for the erasable type. Generally, the film is formed on the transparent substrate by a dry method such as sputtering, etc., under high vacuum.

The moisture absorbency and the water permeability cause the problem of warping of the substrate itself, due to expansion when it absorbs moisture on one hand, and on the other hand, it causes the corrosion of the recording medium by the permeation of water through the substrate, and it shortens the life of the optical disc.

Concerning the heat resistance of the resin for the substrate, there is following problem. Namely, in the optical disc, especially in the write once type or in the erasable type, the temperature of the recording medium becomes 200 °C or higher, during the writing - in or erasing of the records. Therefore, although this heat is not directly applied to the disc substrate, we can estimate that the substrate will become quite hot during the writing or erasing of records. Therefore, if the resin has a low heat resistance, the substrate can be deformed, or the grooves can be deformed, and this is a problem.

On the other hand, the production process of the optical disc often includes the heat treatment process, in order to prevent changes in the substrate or the recording medium with the passing of time. If it is desired to improve the productivity, it should be

treated at as high as possible a treating temperature, so that the treatment time can be shortened. If the heat resistance of the resin is low, the high treatment temperature can not be applied, and the productivity can not be increased, and this is inconvenient.

For such reasons, the PMMA, which has a low heat resistance, is insufficient to withstand the production process of the optical discs or the high temperature of the use conditions, therefore, in the past, only PC which has a higher heat resistance, has been studied as the material to be used for the transparent substrate. However, even PC is not necessarily considered to have sufficient heat resistance, and the resin material which can give higher heat resistance, has been desired.

The method based on Patent Application Kokai No. S63-43910, and which uses the poly vinyl cyclo hexane type resin as the optical disc substrate, has been suggested as the one which can supplement the disadvantages of the existing resins such as PC or PMMA, etc.

[Problem That this Invention Intends to Solve]

However, even in the case when the poly vinyl cyclo hexane type resin is used, the optical disc substrate with good characteristics can not always be obtained, and it is unsatisfactory in some respects, and that is the present situation.

The inventors of this invention studied the forming ability, etc., of the optical disc substrate that uses the poly vinyl cyclo hexane type resin that was suggested in the above mentioned Patent Application, and as the result, they discovered the following.

Poly vinyl cyclo hexane type resin is normally obtained by hydrogenating the aromatic ring of the vinyl aromatic type polymer, and it is a resin that is known as a brittle polymer, the same as poly styrene.

As was mentioned above, the optical disc for the write once type or erasable type discs, receive quite a lot of heat experiences in the conditions under which they are used, and in the production process, therefore, the high heat resistance is required for the resin substrate. Also, as the resin material for the disc substrate, it needs at least enough toughness so that it does not break when it is parted from the mold during the injection molding.

On the other hand, the optical disc substrate must be such that the warping or deformity is rare, and such that the grooves transcription ability must be good, and from such a view point, the fluid ability of the resin during the injection molding time must be as good as possible. Also, to prevent the generation of silver streaks or coloring, the moisture absorption must be decreased, and at the same time, the deterioration of the resin must be prevented as much as possible.

Concerning the poly vinyl cyclo hexane type resin which has a molecular weight with which certain amount of toughness can be maintained, the deterioration of the resin can be prevented in the injection molding at low temperature, but the fluid ability becomes insufficient, therefore, the forming temperature must be raised. The preferred temperature for forming is in the range of 270 to 330 °C, more preferably 280 to 320 °C.

However, in the above mentioned temperature range, the deterioration of the poly vinyl cyclo hexane type resin is inevitable, and the stabilizer must be used.

The objective of this invention is to offer the optical disc substrate with good characteristics consisting of the poly vinyl cyclo hexane type resin, in which the characteristics such as the heat resistance, the toughness, the fluid ability, the moisture absorbency, the transparency, etc., are improved, by adding the stabilizer.

[Method and Operation to Solve the Problem]

The optical disc substrate of this invention is characterized by the fact that it consists of the poly vinyl cyclo hexane type resin which is blended with a hindered phenol type heat stabilizer and a phosphorus type heat stabilizer, of which the 5 % weight loss temperature measured by the thermo gravimetric analyzer is 295 °C or higher.

In other words, the inventors of this invention studied the stabilizer which can effectively prevent the heat deterioration of the above mentioned poly vinyl cyclo hexane type resin, and as the result, they discovered that the deterioration of the resin can be effectively prevented, and the problems such as the silver streaks or coloring, can be eliminated, by co-using a hindered phenol type heat stabilizer and a phosphorus type heat stabilizer, of which the 5 % weight loss temperature measured by the thermo gravimetric analyzer is 295 °C or higher, as the stabilizer, and this invention was made.

In this invention, the preferred hindered phenol type heat stabilizer should have 4 or more hindered phenol groups per molecule.

Also, the preferred phosphorus type heat stabilizer is, tetra kis (2, 4- di- t- butyl phenyl) - 4, 4'- bi-phenylene phosphonite and / or bis (2, 6- di- t- butyl -4- methyl phenyl) penta erythritol -di- phosphite.

In addition, the number average molecular weight of the poly vinyl cyclo hexane type resin is preferably 40,000 to 300,000.

Next, this Invention Will Be Explained in Detail.

The poly vinyl cyclo hexane type resin that is used in this invention is obtained preferably by hydrogenating the nucleus of the styrene type resin (styrene type polymer).

The vinyl aromatic hydrocarbon polymer or the vinyl aromatic hydrocarbon block co-

polymer can be listed as the raw material styrene type polymer. The one which consists of the vinyl aromatic hydrocarbon polymer segment (from now on, this will be abbreviated as segment A.) and at least one or more conjugate diene polymer segments (from now on, this will be abbreviated as segment B.), can be listed as the later vinyl aromatic hydrocarbon block co-polymer.

Styrene, p- methyl styrene, α - methyl styrene, etc., can be listed as the monomers that can be used as the monomer, and especially styrene can be listed as the desirable representative.

The homo polymer which consists of one kind of vinyl aromatic hydrocarbon, or the co-polymer which consists of two or more, can be listed as the vinyl aromatic hydrocarbon polymer. Especially, in the case when the adhesive ability is required, it is preferred to use the co-polymer that can be obtained by co-polymerizing the above mentioned vinyl aromatic hydrocarbon and the unsaturated monomer which has a polar group and which can co-polymerize with the said vinyl aromatic hydrocarbon, in the range in which the characteristics of the vinyl aromatic hydrocarbon polymer will not be impaired.

Next, a similar one to the above mentioned vinyl aromatic hydrocarbon polymer can be listed as the A segment of the vinyl aromatic hydrocarbon block co-polymer. The conjugate diene of the B segment in the block co-polymer is, for example, 1, 3-butadiene, isoprene, 2, 3- di-methyl -1, 3- butadiene, 1, 3- penta diene, 1, 3 - hexa diene, etc., and especially, 1, 3- butadiene and isoprene are common. The block co-polymer consisting of the A segment and the B segment, can be easily obtained by the already known method such as the "living" anion polymerization, for example the method in which polymerization is performed in a hydrocarbon solvent such as hexane, heptane, etc., using an organic lithium compound as the initiator. The content of the A segment in the block co-polymer should be 80 wt % or more, preferably 90 wt % or more, and more preferably it should be 93 wt % or more. If the content of the A

segment is less than 80 wt %, the heat resistance of the resin that is obtained after hydrogenation, decreases, and it becomes unsuitable to be used as the optical disc substrate.

In this invention, the molecular weight of the raw material styrene type polymer should be preferably 50,000 or higher. If the molecular weight of the styrene co-polymer is too low, the heat resistance and the toughness of the resin that is obtained after hydrogenation, decrease.

The decrease in the toughness accompanying the decrease in the molecular weight, is more obvious in those cases in which the content of diene type polymer in the polymer is less. Therefore, the polymer that does not contain the diene type polymer, should have preferably a number average molecular weight of 80,000 or higher. Concerning the upper limit of the molecular weight, there is no particular limit, however, normally, it should be 400,000 or lower preferably.

Poly vinyl cyclo hexane type resin can be obtained by nucleus - hydrogenation of the styrene type polymer like this, in the presence of a hydrogenation catalyst which has the ability to hydrogenate the aromatic hydrocarbons. The hydrogenation catalyst which can be used here, is for example, metals such as nickel, cobalt, ruthenium, rhodium, platinum, palladium, etc., and their oxides, salts, complexes, and those where these materials are supported by the carriers such as activated charcoal, diatomaceous earth, alumina, etc. Among these, Raney nickel, Raney cobalt, stabilized nickel, and the ruthenium, rhodium, or platinum catalysts supported by carbon or alumina, are preferred for their reactivity.

The nucleus - hydrogenation reaction should be carried out preferably under a pressure of 50 to 250 kg / cm², and at a temperature of 100 to 200 °C, using the saturated hydrocarbon type solvent such as cyclo hexane, methyl cyclo hexane, n-octane,

decalin, naphtha, etc.

Here, normally, in the nucleus - hydrogenation of the styrene type polymer, the molecular chain of the polymer is cut as the sub reaction. In order to prevent this molecular chain cutting, the hydrogenation should be done with as high as possible a pressure of hydrogen, and also, it should be done in a short time.

The nucleus - hydrogenation ratio of the aromatic nucleus by the nucleus - hydrogenation reaction should be 90 % or higher, especially 95 % or higher is preferred. If the nucleus hydrogenation ratio is low, less than 90 %, the heat resistance of the resin that is obtained, decreases, and the birefringence increases, and these are problems. Here, in this invention, the heat resistance of the resin should be such that the softening point measured by the thermo mechanical analyzer is 150 °C or higher. Concerning the birefringence, the preferred one is such that when it is formed as the optical disc substrate, the value of $\Delta n_{5.5}$ which will be explained later, becomes 30 nm or less.

In this invention, the molecular weight of the poly vinyl cyclo hexane type resin that is obtained like this, depends on the composition and the molecular weight of the styrene type polymer that becomes the raw material, and the hydrogenation conditions, etc., and also its suitable range varies depending on the composition, however, normally, it should be 30,000 or higher in the number average molecular weight, and preferably it should be 50,000 or higher. From the view point of toughness, the smaller the content of diene type polymer is, the higher the molecular weight is required. If it does not include the diene type polymer, the molecular weight must be 40,000 or higher, preferably it should be 60,000 or higher. The upper limit of the molecular weight is determined from the view point of the forming ability, and normally, it should be 300,000 or less in the number average molecular weight.

In this invention, at least one hindered phenol type heat stabilizer, of which the 5 % weight loss temperature measured by the thermo gravimetric analyzer under an air flow is 295 °C or higher, and at least one phosphorus type heat stabilizer, of which the 5 % weight loss temperature is also 295 °C or higher in same way, are combined and they are blended as the stabilizer, into the poly vinyl cyclo hexane type resin like this.

Here, in this invention, the 5 % weight loss temperature measured by the thermo gravimetric analyzer under an air flow, means the temperature at which the weight loss became 5.0 wt %, when the weight loss was measured while it was heated at a temperature increase rate of 20 °C / min, under an air flow of 100 mL / min.

Those that can be listed as the hindered phenol type heat stabilizer that can be used in this invention, are for example, tetra kis [methylene -3- (3, 5- di- t- butyl -4- hydroxy phenyl) propionate methane, 3, 9- bis [1, 1 - di-methyl -2-{β - (3- t- butyl -4- hydroxy -5- methyl phenyl) propionyl oxy} ethyl] -2, 4, 8, 10- tetra oxa spiro [5, 5] undecane, 1, 3, 5 - tris (3, 5 -di- t- butyl -4- hydroxy benzine -s- tri azine - 2, 4, 6 (1H, 3H, 5H) - trion, and 1, 3, 5- tri methyl - 2, 4, 6- tris (3, 5- di- t- butyl -4- hydroxy benzyl) benzene, etc.

Those that can be listed as the phosphorus type heat stabilizer are, tetra kis (2, 4- di- t- butyl phenyl) -4, 4- bi-phenylene phosphonite, bis (2, 6- di- t- butyl -4- methyl phenyl) penta erythritol -di- phosphite, etc.

Among these stabilizers, as the hindered phenol type stabilizer, the best effect can be obtained when those which have 4 or more hindered phenol groups per molecule, are used.

The suitable amount of these stabilizers to be added, is 0.01 to 3 weight parts each of the hindered phenol type heat stabilizer and the phosphorus type heat stabilizer per 100 weight parts of poly vinyl cyclo hexane type resin, preferably it should be 0.05 to 1

weight parts. If the added amount of the stabilizer is less than this range, the deterioration prevention effect is insufficient, and if the added amount exceeds this range, sometimes bleeding occurs, and the transparency that is necessary for the optical disc substrate, decreases, and these are problems.

The method to mix these stabilizers with the poly vinyl cyclo hexane type resin, is not particularly limited. Normally, the resin and stabilizer are mixed by a ribbon blender, a tumbler blender, a Henshel mixer, etc., and thereafter, it is melt - mulled by a Banbury mixer, a single axis extruder, a twin axis extruder, etc., and it is pelletized. Thus, the pellets obtained like this, are formed by injection molding with a forming temperature of 270 to 330 °C, preferably 280 to 320 °C, and the optical disc substrate which has excellent transparency, and excellent heat resistance, and which is colorless and also in which the optical deformity is extremely small, can be obtained.

The following method, etc., can be used in order to produce the optical disc using the optical disc substrate of this invention; the film of the above mentioned recording medium is formed on the surface of the said substrate by the metal vapor deposition, etc., or the film of an organic color type material is applied by coating, etc., and thereafter, they are covered with a protection film.

[Actual Examples]

Next, this invention will be explained in more detail, referring to the actual examples and comparisons, however, this invention will not be limited to these examples, as long as it does not go beyond its essential scope.

The various physical properties in the Examples and Comparisons were measured by the following methods.

(1) Number average molecular weight:

This was measured the same as poly styrene by gel permeation chromatography

(GPC) using THF as the solvent, and the poly styrene converted number average molecular weight was obtained.

(2) Nucleus hydrogenation ratio (%) :

Poly vinyl cyclo hexane type resin was dissolved in tetra hydro furan (THF), and it was measured by UV absorption.

(3) Softening point (°C) :

The softening point was measured at a temperature increase rate of 5 °C / min, using the thermo mechanical analyzer made by Dupont Co.

(4) Light transmission ratio of the optical disc substrate (%) :

This was measured according to JIS K 6714.

(5) Birefringence (nm) of the optical disc substrate:

This was evaluated by the birefringence of the formed disc of which the thickness is 1.2 mm and the diameter is 130 mm, at the position that is 5.5 cm from the center of the disc. (from now on, this will be abbreviated as $\Delta n_{5.5}$.) The birefringence was measured by a polarizing microscope made by Nihon Kogakusha K.K.

(6) Warpage (mm) of the optical disc substrate:

This was measured by using a flatness tester FT-7 made by NiDEK Co.

(7) Appearance of the optical disc substrate:

The coloring or the generation of silver streaks, etc., were visually examined for the optical disc substrate that was formed by the method described below.

Example 1

0.2 weight parts of tetra kis [methylene -3- (3, 5- di-t - butyl -4- hydroxy phenyl) propionate methane ("Irganox 1010" made by Japan Ciba Geigy Co.), and 0.2 weight parts of tetra kis (2, 4 - di-t-butyl phenyl) -4, 4'- bi-phenylene phosphonite ("Irgaphos P-EPQ" made by Japan Ciba Geigy Co.), were added into 100 weight parts of poly vinyl cyclo hexane which was obtained by hydrogenating the styrene homo polymer, and of which the number average molecular weight is 70,000, and the nucleus hydrogenation ratio is 99 %, and it was melt - mulled at 260 °C, using an extruder.

Using the injection molding machine (MI40A, made by each company or by Kakuki K.K.), these pellets were formed into an optical disc substrate of a 1.2 mm thick disc with a 130 mm diameter, at a resin temperature of 300 °C, applying a stanbar? (*phonetically written, Translator*) with grooves on the movable die side.

Table 1 shows the physical properties of the optical disc substrate that was obtained.

Example 2

0.2 weight parts of 3, 9 - bis [1, 1 - di-methyl -2- {β -(3-t -butyl -4-hydroxy -5- methyl phenyl) propionyl oxy} ethyl] -2, 4, 8, 10 tetra oxy spiro [5, 5] undecane ("Mark Aφ-80" made by Adeca? Argas? Co.) and 0.2 weight parts of tetra kis (2, 4 - di-t-butyl phenyl) -4, 4'- bi-phenylene phosphonite ("Irgaphos P-EPQ" made by Japan Ciba Geigy Co.), were added into 100 weight parts of poly vinyl cyclo hexane type resin, which was obtained by hydrogenating the styrene - butadiene - styrene block co-polymer (butadiene content of 5 wt %) that was produced by anionic polymerization, and of which the number average molecular weight was 60,000, and the nucleus hydrogenation ratio was 99 %, and it was pelletized and injection molded the same as in Example 1.

Table 1 shows the physical properties of the optical disc substrate that was obtained.

Comparison 1

The optical disc substrate was obtained in the same way as in Example 1, except that 0.2 weight parts of butyl hydroxy toluene was used as the stabilizer, and that the injection molding temperature was made to be 260 °C.

Table 1 shows the physical properties of the optical disc substrate that was obtained.

Comparison 2

The optical disc substrate was obtained in the same way as in Example 1, except that 0.2 weight parts of di-stearyl thio propionate was added instead of the "Irgaphos P-EPQ".

Table 1 shows the physical properties of the optical disc substrate that was obtained.

As is clear from Table 1, when the poly vinyl cyclo hexane type resin, in which the specific hindered phenol type heat stabilizer and the phosphorus type heat stabilizer are blended, is used, the improved characteristics optical disc substrate which has excellent heat resistance, transparency, optical characteristics and shape stability, and which does not have the silver streaks or coloring, can be obtained. Compared with that, Comparison 1 had a slight amount of coloring and the generation of silver streaking, although the softening point of the disc or the transparency did not change. The warping was 0.5 mm, and the birefringence was high, $\Delta n_{5.5} = 8 \text{ nm}$. Comparison 2 showed the coloring (yellow), and the silver streaks appeared slightly.

Table 1

| | | Example | Comparison |
|--|--|---------|------------|
| | | | |

| | | 1 | 2 | 1 | 2 |
|----|---------------------------------|--------|--------|--------------|--------------|
| * | Number average molecular weight | 70,000 | 60,000 | 70,000 | 70,000 |
| | Nucleus hydrogenation ratio (%) | 99 | 99 | 99 | 99 |
| | Softening temperature (°C) | 172 | 165 | 172 | 167 |
| ** | Light transmittance (%) | 90 | 90 | 90 | 89 |
| | Birefringence (nm) | 3 | 3 | 8 | 3 |
| | Warping (mm) | ≤0.10 | ≤0.10 | 0.5 | ≤0.10 |
| | Silver streak | no | no | slightly yes | slightly yes |
| | Coloring | no | no | slightly yes | yes |

* Resin

** Optical disc substrate

[Effect of the Invention]

As was mentioned above, this invention can offer the optical disc substrate which does not have the problem of resin deterioration, and which can be produced stably, from the excellent characteristics poly vinyl cyclo hexane resin which has excellent heat resistance, high transparency, and of which the moisture absorbency is low, and the birefringence is low.

In this invention, an especially great effect can be obtained, when the hindered phenol type heat stabilizer which has 4 or more hindered phenol groups per molecule, is used, and the tetra kis (2, 4- di- t- butyl phenyl) -4, 4'- bi-phenylene phosphonite and / or bis (2, 6- di- t- butyl -4- methyl phenyl) penta erythritol -di- phosphite is used as the phosphorus type heat stabilizer, and also when the number average molecular weight of the poly vinyl cyclo hexane type resin is 40,000 to 300,000.